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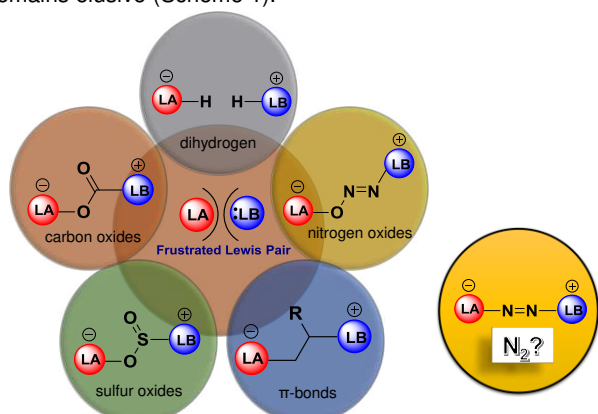


A Step Closer to Metal-Free Dinitrogen Activation: A New Chapter in the Chemistry of Frustrated Lewis Pairs

Rebecca L. Melen*[a]

Over the last century, the activation of small molecules has been almost exclusively associated with transition metals. Indeed, the versatility and *savoir-faire* of *d*-block metals have rendered them indispensable for a vast number of catalytic transformations such as the activation of small molecules e.g. H_2 , CO_x , NO_x and more interestingly, N_2 . Found in many biomolecules, nitrogen is an essential element needed to sustain life. Despite its abundance in the atmosphere, activation of nitrogen remains a huge challenge both in the laboratory and on an industrial scale owing to the high $N\equiv N$ triple bond strength. While nitrogen fixation in biological systems is known to occur at room temperature by nitrogenase enzymes, the production of ammonia from the reduction of dinitrogen remains one of the most challenging, yet important, processes in industry which requires very forcing conditions. Most notably, the Haber-Bosch process accounts for 1–2% of the annual global energy supply in the synthesis of ammonia for fertilizers from elemental nitrogen. Recently, several groups have published work using a biomimetic approach to N_2 activation whereby active sites of nitrogenases are mimicked outside the native enzyme. While many examples of Fe-Mo-type systems have been shown to bind and reduce dinitrogen,^[1] other simpler single metal catalysts have begun to take precedence in the transition metal field.

A major revelation however was reported in 2006 when a metal-free compound that can reversibly activate hydrogen was reported.^[2] From this discovery, the field of frustrated Lewis pair (FLP) chemistry was born which has heralded a paradigm shift in main group chemistry. Owing to the presence of unquenched Lewis acidic (electrophilic) and basic (nucleophilic) sites, these compounds may represent the frontier orbitals of transition metal catalysts which have the ability both to accept and donate electrons. This feature allows FLPs to be active in a wide range of small molecule activation reactions which encompass gaseous molecules including *inter alia* dihydrogen, carbon oxides, nitrogen oxides and sulfur oxides as well as π -bonds.^[3] One notable absence however is the metal-free activation of N_2 which still remains elusive (Scheme 1).

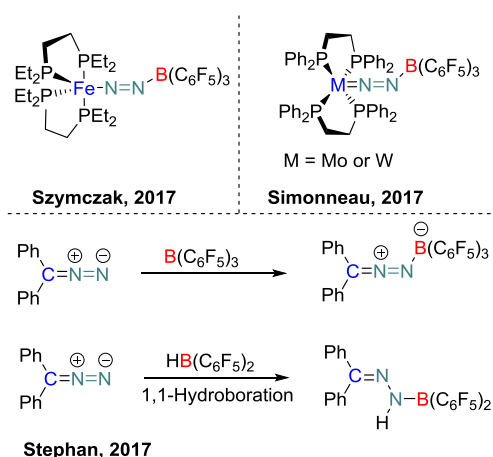


Scheme 1 Frustrated Lewis pair activation of small molecules.

The possibility of metal-free activation of N_2 has been a topic of speculation over recent years, with many ponderings over both the feasibility and design of systems that possess the ability to

activate such a strong bond. However, the thought of metal-free H_2 activation would have also appeared to be far-fetched a mere 15 years ago therefore, with breakthroughs in main group chemistry over the past few years, the notion of direct metal-free N_2 reduction is not such an obscure thought.

Toward the activation of small molecules, boranes, specifically tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$ and related fluorinated derivatives, are one class of main group compounds that has gained popularity over recent years. Owing to their high Lewis acidity and steric bulk they have been widely employed in FLP chemistry as well as Lewis acid catalysis.⁴ However, it was only earlier this year that tris(pentafluorophenyl)borane was found to interact with transition metal N_2 complexes by the groups of Szymczak^[5] and Simonneau^[6] (Scheme 2, top). Szymczak demonstrated an N_2 activation strategy based upon the use of the strong Lewis acid $B(C_6F_5)_3$ to weaken the $N-N$ bond in Fe- N_2 complexes in a “push-pull” fashion. This mimics the “push-pull” hypothesis for nitrogenase active sites which employs a reduced iron center to push electron density into the N_2 fragment as well as Lewis acidic sulfur-bound protons to pull electron density from the N_2 fragment in a bid to overcome the high barrier to the initial hydrogenation of N_2 .^[7] This synergistic effect to weaken the nitrogen-nitrogen bond was subsequently likened to an FLP mechanism by Simonneau in which the “push” effect was provided by the Lewis base component of an FLP (a low valent Group 6 metal) and the “pull” effect was mimicked using the Lewis acid component of an FLP ($B(C_6F_5)_3$). In the former case, Szymczak showed that $B(C_6F_5)_3$ can activate the $N-N$ bond for protonation whereas Simonneau showed that the borane activated Group 6 metal- N_2 complex can be subjected to hydroboration or hydrosilylation. These results represent a significant leap in FLP chemistry indicating that an FLP mode for activation of N_2 is certainly possible.

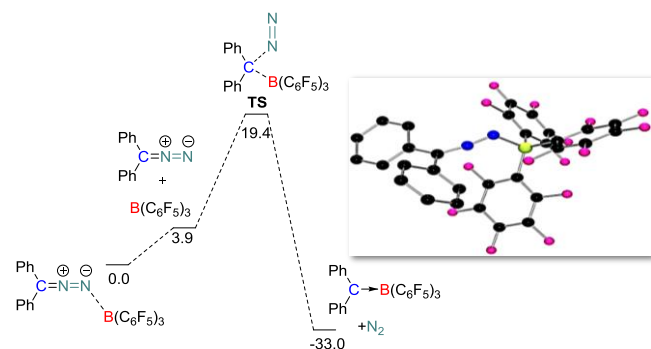


Scheme 2 Work in 2017 on Lewis acidic boranes for $N-N$ bond activation.

The next challenge is to remove the metal altogether, a challenge which remains elusive although, the binding of N_2 to Lewis acids has been the focus of a number of computational studies. In addition to this, a $(N_2)BF_3$ species can be transiently generated and characterized spectroscopically through supersonic expansion at 170 K and at 600 torr which indicates that metal-free N_2 activation is potentially achievable.^[8] Recently, the article entitled “1,1-Hydroboration and Borane Adduct of Diphenyldiazomethane: A Prelude to FLP- N_2 Chemistry?” was

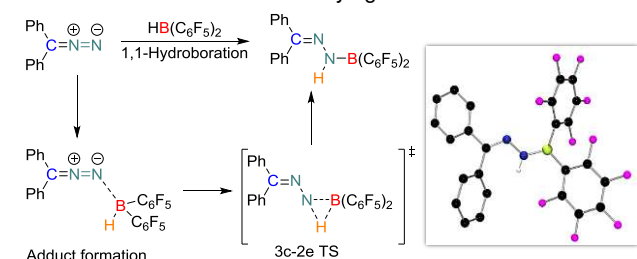
[a] Dr. R.L. Melen
School of Chemistry
Cardiff University
Main Building, Park Place, Cardiff, Cymru/Wales, CF10 3AT(UK)
E-mail: MelenR@cardiff.ac.uk

published by Stephan *et al.* (Scheme 2, bottom) which moves the activation of N₂ in a metal-free manner a step closer to realization.⁹ Diazo compounds are highly reactive yet useful building blocks in organic synthesis and have been widely used in a multitude of transformations as versatile intermediates. As reagents, they have the benefit of being clean, with the elimination of N₂ as the only by-product to liberate carbenes. However, their use in main group chemistry is under-represented although the B–C insertion reactions of B(C₆F₅)₃ are known.¹⁰ In this report by Stephan, diphenyldiazomethane is shown to react with the Lewis acidic boranes B(C₆F₅)₃ and HB(C₆F₅)₂ initially through adduct formation. This generates similar intermediates to those observed by Szymczak and Simonneau in which the N₂ fragment can be considered as being bound between a Lewis base and a Lewis acid. In the former case, the reaction with B(C₆F₅)₃, the adduct with diphenyldiazomethane proved to be highly unstable and rapidly evolved N₂ gas at room temperature. However, low temperature studies allowed the adduct to be isolated in moderate yields. Multinuclear NMR spectroscopy confirmed adduct formation in addition to crystallographic studies showing C–N and N–N double bond character of the C=N=N–B unit, reminiscent of the M=N=N–B moieties observed for the B(C₆F₅)₃ adducts reported with Fe, Mo and W. However, the N–B bond in the diphenyldiazomethane adduct is significantly longer, and therefore weaker, than those reported for the metal complexes.



Scheme 3 B(C₆F₅)₃ adduct with diphenyldiazomethane (insert) and the calculated degradation pathway. Relative free energies are indicated in kcal·mol⁻¹.

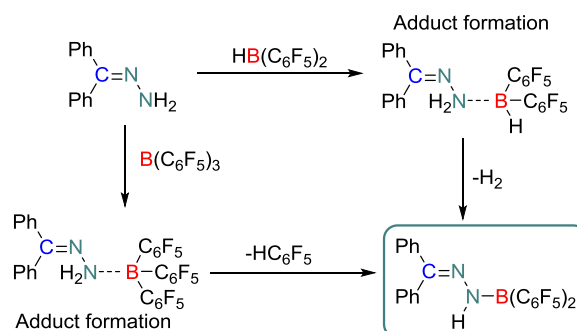
With Piers' borane, HB(C₆F₅)₂, an unprecedented 1,1-hydroboration reaction of the N–N bond resulted (Scheme 4). Typically hydroboration reactions generate the *syn*-1,2-addition product however, the unusual 1,1-pathway observed here can be attributed to the migration of hydrogen from boron to the proximal nitrogen atom. Probing this mechanism computationally revealed an early transition state reminiscent of a 3-center, 2-electron bond for the B–H–N unit with a B–H bond order of 0.54 and an N–H bond order of 0.33. This infers the donation of electron density from the B–H bond into the low-lying π* orbital on the N=N unit.



Scheme 4 Proposed mechanism of the 1,1-hydroboration of diphenyldiazomethane to yield Ph₂C=NN(H)B(C₆F₅)₂ (insert).

Parallel studies with Ph₂CNNH₂ and either B(C₆F₅)₃ or HB(C₆F₅)₂ were also shown initially to yield the Lewis acid-base adducts (Ph₂CNNH₂)B(C₆F₅)₃ or (Ph₂CNNH₂)HB(C₆F₅)₂ respectively. Upon heating, both of these compounds generate the same product seen earlier from the 1,1-hydroboration of

diphenyldiazomethane with HB(C₆F₅)₂ either from the loss of HC₆F₅ or H₂ (Scheme 5).



Scheme 5 Reactions of Ph₂CNNH₂ and either B(C₆F₅)₃ or HB(C₆F₅)₂.

2017 has seen great advancements in the use of FLPs to activate dinitrogen towards protonation or hydrosilylation and hydroboration. The presented systems use electron-rich Lewis basic metals to “push” electron density into the N₂ unit and employ the strong Lewis acid B(C₆F₅)₃ to “pull” electron density from N₂ thereby synergistically weakening the N–N bond. The increasing focus on chemical transformations and the utility of main group species however poses the question: could transition metals be circumvented altogether? This trendsetting research by Stephan clearly implies that the metal-free activation of N₂ may be achievable in the not too distant future and provides a fresh target for the field of FLPs. It is likely that in the next few years a metal-free system capable of activation and functionalization of dinitrogen will be uncovered. Such a finding would further cement the importance of main group chemistry in the activation of small molecules.

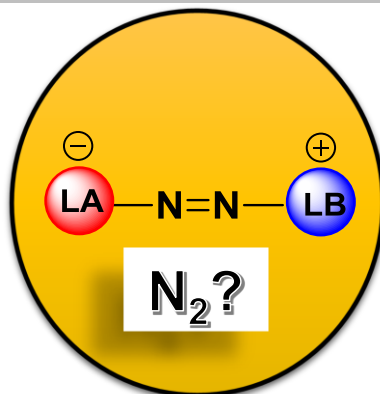
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HIGHLIGHT

The increasing focus on small molecule activation and chemical transformations of main group species poses the question: could metal catalysts be circumvented altogether in the activation of dinitrogen? This ground breaking research by Stephan clearly implies that the metal-free activation of N_2 may be achievable in the not too distant future and provides a fresh perspective to the field of FLPs.



*Rebecca L. Melen**

**Foreshadowing a New Chapter in
FLP Chemistry? A Step Closer to
Metal-Free Dinitrogen Activation.**